Material Science and Technology
Nanoscience

The Role of Carbon Surface Diffusion on the Growth of Epitaxial Graphene on SiC

Graphene monolayers hold considerable promise in nanoscale electronics if the growth mechanisms can be controlled .

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Graphene is the thinnest material ever known. It is a single atomic layer of carbon (graphite), and because of its excellent electronic, thermal, and mechanical properties, there has been considerable research concerning applications in nanoscale electronics. One of the biggest challenges in developing graphene-based electronics is how to synthesize it. Furthermore, to be useful in nanoelectronics, the synthesis method has to be scalable to produce graphene films the size of standard semiconductor wafers, at least a few inches in diameter. In general, good quality carbon-based materials are produced in high-temperature or high-pressure environments. These harsh environments restrict the options of material synthesis, and limit a deeper understanding of growth processes. Thus controlling growth of a one-atom-thick film over square-inches of area presents many challenges.

Graphene growth on a silicon carbide (SiC) substrate is regarded as one of the promising ways to achieve graphene-based electronics. When SiC is heated, sublimation of Si takes place, leaving behind carbon atoms which assemble ("graphitize") into graphene layers. Recently, it was found that heating SiC in argon at atmospheric pressure leads to significant improvements in size, film thickness, and electronic properties compared to heating SiC in vacuum. However, to gain better control and to further improve the quality of the graphene films, a comprehensive understanding of the growth processes and kinetic pathways is needed.

Using various microscopy techniques, researchers at Sandia have studied the transient stage when the first graphene layer is growing. Figure 1 shows the surface topography of a partially-grown graphene film displaying three distinct growth features as illustrated in the 3D insets. From the phase contrast image (right), one can identify the materials covering the surface: graphene films and so-called buffer layers
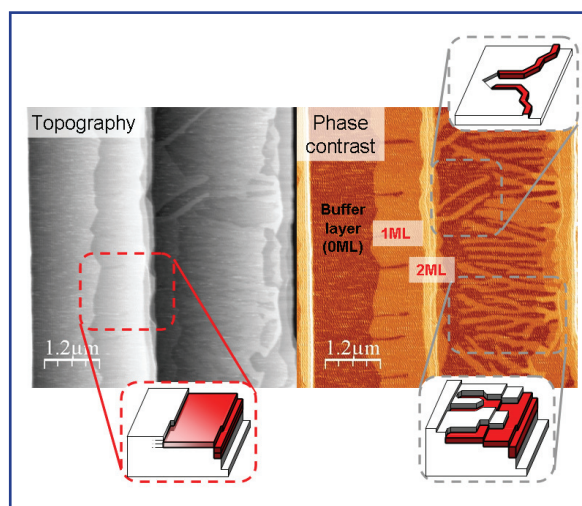

Figure 1: Morphology of SiC surfaces with growing graphene layers, acquired using atomic force microscopy (AFM). The left image is topography (grey scale), and the right image is the phase contrast (red-to-white scale). The steps go down from left to right. Phase contrast imaging is sensitive to the mechanical response of the material surface, and therefore is used as a fingerprint to distinguish a single graphene layer (1 ML), two layers (2 ML), and the interface layer formed during graphitization. Three distinct growth features are highlighted and schematically illustrated in the 3D insets, where the surfaces colored in red are terminated by graphene layers, and the ones in white are buffer layers (also indicated in the phase image). The surface composition is independently determined using LEEM, whose image contrast depends on the electronic structure of the material at the surface.
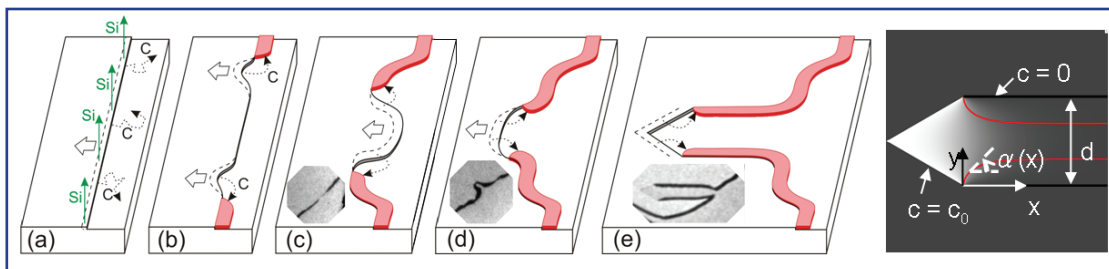
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Figure 2: Schematics of the formation of an arrow feature and the calculated surface carbon atom concentration map. The process starts with sublimation of silicon atoms and formation of carbon atoms at the step edge (a). Once small patches of graphene are formed at the step edge, they grow in to ribbons of graphene decorating the step edges (b, c). When two ribbons meet, they turn and grow into the terrace given the limited number of carbon atoms emitted from the undecorated step edge (d, e). Some intermediate states have been detected in LEEM (insets in c-e) supporting this scenario. The LEEM images are (c) 2x2 μm^2, (d) 2x2 μm^2, and (e) 4x2 μm^2. The surface carbon atom concentration shown in the far right image is calculated by solving the time-dependent diffusion equation for the arrow geometry. The white area denotes higher carbon atom concentration. The red lines are the calculated boundaries of the resulting graphene ribbons, reproducing the experimentally-observed shape.

(precursor of a graphene film) separated by the atomic steps. The atomic steps originate from atomic-scale misalignment of a crystal plane and the polished substrate, commonly found on monolithic crystal surfaces. The left 3D inset (with a red boundary) features "step-flow growth" that turns three units of SiC into one layer (1 ML) of graphene. The right insets (with grey boundaries) are an "arrow feature" (up) and a "finger feature" (down) developed at the single atomic steps of SiC.

The analysis of "arrow features" provides much insight into how carbon diffuses on the surface during the synthesis process. Based on the surface topography surrounding arrow features, the sequence of its formation was deduced (details in Figure 2). The growth of arrow features (or the elongation of the shaft) can also be described analytically by solving the diffusion equation in an arrow geometry (far right in Figure 2). This reproduces the final geometry of an arrow feature, and shows the development of the concentration gradient of the surface carbon atoms inside an arrow shape during the growth. It also means that the diffusion of carbon atoms emitted at the atomic steps of buffer layer surfaces is the key factor in shaping the unique arrow geometry. Unfortunately, the diffusion-driven growth process leads to an unfavorable film morphology that cannot be controlled.

An entirely different mechanism is happening in "step-flow growth," which converts three units of SiC to 1 ML of graphene. This mechanism was captured by a low-energy electron microscope (LEEM) in real-time at elevated temperature (details in Figure 3). The clear boundary between buffer layers and 1 ML of graphene, and the evolution of the boundaries, indicates that buffer layers are transformed to 1 ML graphene at the boundaries (as depicted schematically in the right illustration in Figure 3). Unlike the arrow feature, step-flow growth does not involve much carbon diffusion because carbon atoms emitted at the growth fronts are immediately turned into a graphene layer. Most importantly, step-flow growth creates homogeneous uninterrupted graphene films over a micrometer scale, which is promising for electronic device fabrication.

This work establishes a well-defined spatial relationship between the formation of carbon atom precursors and the growth of graphene. It is set by the starting configuration of the atomic steps of the buffer layer surface. Clearly, step-flow growth is the preferred mechanism to produce large-area graphene films. The next step is to clarify if, and how, different growth mechanisms alter the properties of this one-atom-thick material. Ultimately, the goal is to control the growth over an entire SiC substrate.
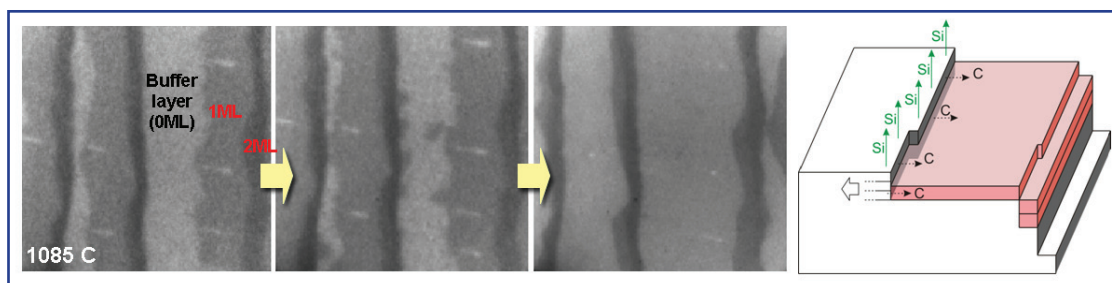

Figure 3: Step-flow growth of graphene. Left images (3.5x3.5 μm^2) were obtained in real time with LEEM. The dark gray regions consist of 2 ML graphene, the medium gray regions are 1 ML, and the light gray regions are buffer layer. The right schematic illustrates the topography of step-flow growth. Triple bilayers of SiC (dotted lines) are transformed into 1 ML graphene.